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ADAPTATION OF WATER PRECONCENTRATION TECHNIQUES FOR TRACE METAL DETECTION. B.R. Hollebone, E. Dowdall\*, K.L. Singfield, L.J. Brownlee, Department of Chemistry, Carleton University, Ottawa, Ontario, K1S 5B6; P. Vijan, Laboratory Services Branch, MOE.

### Introduction

The overall goal of this project is the design, construction and verification of a water sampler for the preconcentration of trace metals from raw and treated drinking water, in preparation for analysis by inductively coupled plasma emission spectroscopy (ICPES). This has been approached through the adaptation of an existing preconcentration system for organic pollutants in raw and treated water developed in these laboratories, and currently under test by the Ministry of the Environment. A schematic of the water sampler is shown in figure 1.

To use ICPES effectively for water analysis and to take advantage of its simultaneous multi-element capability, simultaneous preconcentration of as many as possible target trace metals is required. The target metals are a group of potentially toxic metals found in raw and treated waters such as aluminum, chromium, cobalt, copper, iron, lead, manganese, mercury, molybdenum, nickel, strontium, vanadium, and zinc. The water samples also contain other metals at much higher concentrations such as sodium, potassium, calcium, and magnesium. In terms of toxic risk, these can be called irrelevant. Their presence, however, can cause serious matrix interferences in ICPES analysis.

Successful trace analysis of heavy metal ions requires the elimination of irrelevant but interfering hard metal ions. In this proposed preconcentration procedure, the separation of the target metals from the irrelevant metals is being achieved through selective adsorption on a modified resin contained in a column. The resin is modified by the addition of a chelating ligand. Essentially, the column can simultaneously provide an adsorbing medium for the target trace metals and an eluting medium for the irrelevant metal ions. Traditional methods involve collection of all metals, followed by the selective elution, coprecipitation or extraction of the metals of interest.

The differentiation of the irrelevant hard and the trace soft metal ions is possible because of their different complexing characteristics. The hard alkali and alkali-earth metals exhibit a preference for a hard donor atom, such as oxygen, for complexation. The soft heavy metals exhibit a preference for a soft donor atom, such as sulfur or nitrogen. Therefore, preferential complexation can be employed to separate hard from soft metals. To ensure that the undesirable metals are continuously eluted during the concentration of the heavy metals, the ligand should have soft nitrogen and sulfur donor atoms preferably used in combination with each other in a polydentate ligand.

The ligand-to-resin bond can be formed by varying the resin type and manipulating the terminal functional group on the ligand, to achieve various binding mechanisms. An adsorbent link

is most applicable for the methodology desired in these studies, which requires fast batchwise resin preparation, flexibility in binding and elution of metals, and choice of elution products. In the desired binding mechanism the bidentate or chelate ligand is hydrophobically adsorbed to the resin to form metal complexes by covalent donor bonds. The adsorption of the ligand to the resin is strengthened by an electrostatic attraction between the hydrophobic aromatic structure of the resin and the hydrophobic aromatic portion of the ligand.

Some commercially available ligands that are possible candidates for the desired extraction are 2-mercaptopyridine, 2-quinolinethiol, 2-mercaptothiazoline and 2-mercaptobenzothiazole. Most recent literature has shown the ability of 8-mercaptoquinoline to preconcentrate micro amounts of elements in natural water. These elements include a wide range of metals from both group II and III.

The type of resin chosen to be tested will be XAD-4. This resin has been successfully used to support hydrophobic chelate ligands which coordinate using either 2 sulphur atoms or 1 sulphur and 1 nitrogen atom<sup>2</sup>.

#### Experimental

The overall design of the trace metals preconcentration instrument is the same as that of the organic sampler. The major

emphasis in adapting the design to one suitable for metal analysis is on the replacement of stainless steel components with Teflon or other organic materials such as nylon, polypropylene or polyethylene.

Initial tests were performed to determine which ligand yielded the optimum ratio of ligand to resin. Other considerations for the choice of ligand were the ease of resin preparation and shelf life of the loaded resin. The ligand chosen was 2-mercaptobenzothiazole (MTB) since a ratio of 0.5 mmol ligand:1 ml resin provided the maximum concentration of ligand complexed on the resin. This ratio presents 2.5 mmol of ligand for every 5 ml of resin. There is sufficient amount of ligand on the XAD to completely complex with the metals since a 40 ppb metal sample in a 25 ml solution represents approximately  $1 \times 10^{-8}$  moles of metal.

Experimentation was performed using glass columns packed with 5 ml of the ligand loaded resin. All materials were soaked in concentrated nitric acid and thoroughly rinsed with deionized/distilled water. A 50 ml cocktail of five heavy metals - cadmium, chromium, zinc, copper and lead (1ug each) - and one of four undesirable metals - potassium, sodium, magnesium or calcium (10 to 300 ppm each) - in deionized/distilled water was applied to the columns. The columns were then washed with 50 ml of deionized/distilled water to simulate actual sampling conditions and to determine the retention of the hard and/or soft metals on the column. The columns were then eluted with 25 ml of

1% nitric acid and the samples were stored in polyethylene bottles. Solutions of methionine or cysteine in 5% nitric acid were also tested as possible eluting agents.

### Results

The initial experiments of the column containing 100 grams of treated resin were performed with a 1 mL test sample containing 1000 ppb of cadmium. After a 50 mL wash and a 1 % nitric acid elution, essentially 90 % recovery was obtained.

Similar conditions were used to test the effects of interferences on five heavy metal ions. The range of interference concentrations used was from 0 to 300 ppm, while the concentration of test metal ions - chromium, copper, zinc, cadmium and lead - was 40 ppb. The results for interferences from magnesium and calcium as functions of their concentrations are shown in figures 2 and 3. Recoveries in the presence of sodium and potassium interferences were not affected significantly compared to interferences by calcium and magnesium.

The recoveries of test ions following elution are variable with and without the presence of interfering ions. Cadmium and lead exhibit approximately 100% recovery in almost all cases while copper, chromium and zinc exhibit much lower recoveries, with the highest recoveries occurring at the lowest concentration of the interfering ions. Copper exhibited the lowest recovery

even in the absence of interfering ions.

The extracts were analyzed for the presence of these interfering ions and none were found, indicating that these ions were not bound to the ligand at the time of elution.

#### Discussion

The adaptation of the dioxin preconcentration sampler to the detection of trace levels of heavy metal ions has involved several major considerations. The first is the conversion of all internal surfaces from stainless steel to inert plastics to minimize the adsorption of metal ions or hydrated metal oxides to any hydrophilic surfaces. Another, is the adaptation of the filtering step to insoluble metal detection. Finally, of much importance, is the development of a suitable ligand for soluble metal ion detection.

The first step is in progress and the fully adapted preconcentration instrument will be functional in the near future. The second step requires only the identification of filter materials similar to those used in the organic sampler which will not interfere with mildly acidic extraction processes required for metals. The filtration step is optional and if desired, the water stream can be taken directly to the adsorption columns to avoid this step. The adaptation of the column adsorbent procedures is the most important feature of this research. Essentially, a technique is being developed to be

transparent to irrelevant ions and thus, selectively capturing the heavy metal ions of interest. The adsorbent is treated with ion selective ligands in an effort to preferentially adsorb the trace ions at the 40 ppb level in a background of 10 to 300 ppm of alkali and alkaline earth metal ions.

The results show that MTB is a very effective chelating agent for some of the test metal ions. It does not appear to bind either the monovalent alkali metal ions or the divalent alkaline earth ions but does appear to bind the target metal ions. This can be deduced from the observed recovery behaviour.

In the absence of interferences, copper, zinc and chromium divalent ions yield low recoveries while those of cadmium and lead tend to be highest, particularly in the absence of interfering ions. This correlates with the very strong bonding of cadmium and lead to sulphur, and the preference of chromium, copper and zinc for bonding to ligands containing oxygen or nitrogen. These latter ions are more easily complexed by either water or the oxygen-containing nitric acid ion than are cadmium and lead. This situation is unchanged in the presence of sodium or potassium because these ions have very weak bonding to sulphur ligands.

Thus, according to the data, it does appear that MBT is effective as a selective chelating agent for the cadmium and lead ions which are most strongly bound by sulphur, from a water matrix, even in the presence of interfering ions. The ions of chromium, copper and zinc are not completely retained for two

reasons. First, in the absence of interfering ions the ligand is not efficient at retaining these metals during the water wash used to remove the interfering ions prior to acid elution. Second, in the presence of interfering ions there is a further "salting out" effect which increases with increasing interference concentrations.

The 1% nitric acid medium is adequate for effective elution of the test ions. In revising the experiments, more retentive ligands must be studied to permit significant capture of the harder copper, chromium and zinc metals. This would require ligands with more readily available thiol groups, replacing the mercapto ligands or possibly amino groups rather than aromatic nitrogen atoms. In any case, the work on this first ligand has provided evidence that the concept of selective trace metal ion capture is viable, and further work to optimize the ligand structure should permit the effective analysis of most toxic metals at or below the ppb level.

#### References:

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FIGURE 2

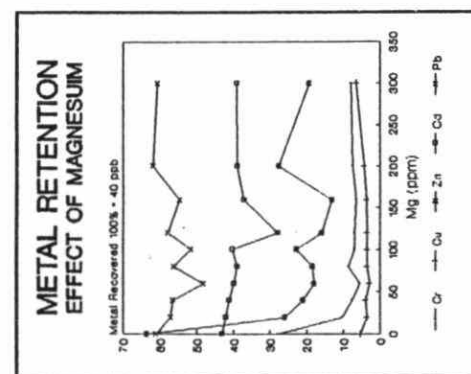


FIGURE 1

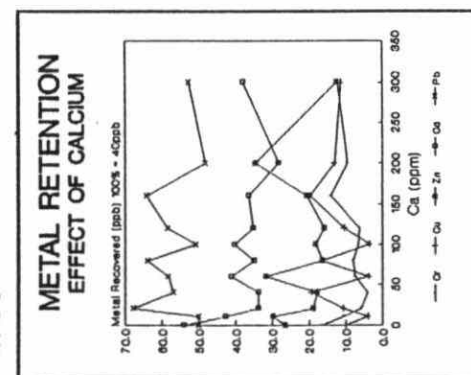
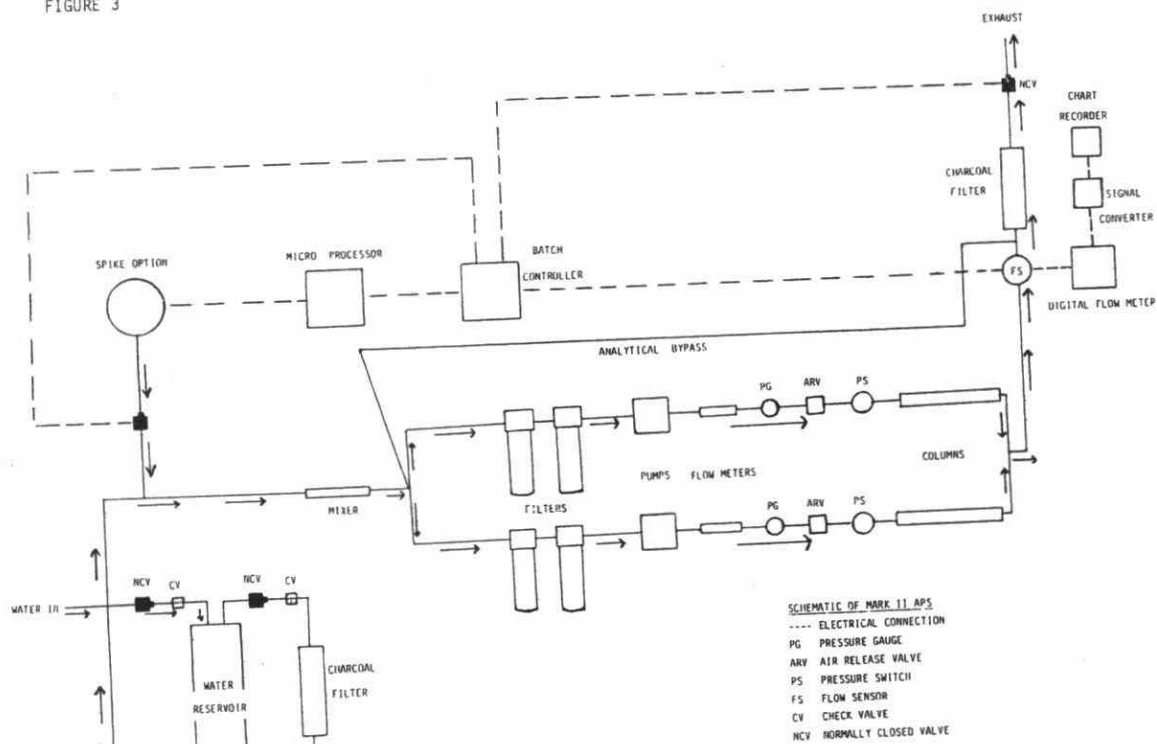


FIGURE 3



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TD/5/T43